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THE DISSOCIATION CONSTANT OF THE  
ORTHO-CHLORO-ANILINIUM ION

BY

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In this paper the dissociation constant of the *o*-chloro-anilinium ion

$$K = (\text{H}^+) (\text{B}) / (\text{BH}^+), \quad (1)$$

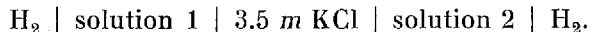
where  $(\text{H}^+)$ ,  $(\text{B})$ , and  $(\text{BH}^+)$  are the concentrations of hydrogen ions, *o*-chloro-aniline, and *o*-chloro-anilinium ions respectively, is measured by means of the glass electrode in the same way as the dissociation constant of the anilinium ion was determined in an earlier paper.<sup>1</sup>

Cells of the following composition were measured



The "solution" was either an *o*-chloro-aniline buffer (solution 1), or a hydrochloric acid solution (solution 2). The analytical composition of solution 1 was:  $a$  molar *o*-chloro-anilinium chloride,  $b$  molar *o*-chloro-aniline,  $(s - a)$  molar sodium chloride, where  $a \cong b$ . Throughout a series of measurements the total salt concentration  $s$  was constant while four different buffer concentrations were used:  $a \cong b \cong 0.025$ , and  $3/4$ ,  $1/2$ , and  $1/4$  of this concentration. Solution 2, which was measured every day, had the composition:  $0.01026 \text{ } m \text{ HCl}$ ,  $0.0900 \text{ } m \text{ NaCl}$ . The difference  $E$  volts between the e. m. f. measured for solutions 1 and 2 may be considered as the e. m. f. of the cell

<sup>1</sup> PEDERSEN, Kgl. Danske Vid. Selsk., Math.-fys. Medd. **14** (1937) no. 9.



In the paper mentioned above it was shown that, while it is in principle impossible to find  $K$  for the actual buffer solutions without making an arbitrary assumption concerning the salt effect potential, we may by extrapolation find  $K$  for sodium chloride solutions containing the buffer constituents in infinite dilution. The values of  $K$  found in this way are independent of both the diffusion and the salt effect potentials.

We use the same symbols as in the earlier paper, and, in addition, the following abbreviations

$$\alpha \equiv \log \frac{f_1}{f_{(\text{NaCl})_1}} - \delta_1 + \delta_{(\text{NaCl})_1} \quad (2)$$

and

$$\beta \equiv \delta_2 - \delta_{(\text{NaCl})_1} - \log (\text{H}^+)_2 - \log \frac{f_2}{f_{(\text{NaCl})_1}}. \quad (3)$$

We then have

$$-\log K - \alpha = \frac{E}{\varrho} + \beta - \log \frac{b + (\text{H}^+)_1}{a - (\text{H}^+)_1}. \quad (4)$$

Throughout a series of measurements at constant salt concentration  $\beta$  is the same. It can be calculated by means of equation 3 from the known hydrogen ion concentration  $(\text{H}^+)_2$  and the data given in the first paper. We are not able to calculate  $\alpha$ , but it disappears when solution 1 is pure sodium chloride solution.  $(\text{H}^+)_1$  and  $(-\log K - \alpha)$  are found from equations 1 and 4 by successive approximation, the final step being the calculation of  $(\text{H}^+)_1$  for each of the buffer solutions from  $a$ ,  $b$ , and the value of  $K$  for  $s$  molar sodium chloride solution given by the expressions 5.  $(\text{H}^+)_1$  is introduced into equation 4, and  $-\log K - \alpha$  is calculated. From a series of values of  $-\log K - \alpha$  corresponding to the same  $s$  but varying  $a$  we find by rectilinear extrapolation  $-\log K - \alpha$  when  $a = 0$ , that is,  $-\log K$  for

an *s* molar sodium chloride solution. The extrapolation is carried out by the method of least squares. Each determination is given a weight proportional to the concentration of the buffer constituents.

The buffer solutions were made from *o*-chloro-anilinium chloride and sodium hydroxide solution. The *o*-chloro-anilinium chloride was prepared from 50 g. *o*-chloro-aniline (The British Drug Houses, Ltd.), which was dissolved in 550 cc. boiling 10% hydrochloric acid. The salt obtained by cooling in ice was recrystallized from 10% hydrochloric acid, washed with water and alcohol, and dried over sulphuric acid (yield 47 g., preparation 1). According to KING and ORTON<sup>1</sup> the salt obtained in this way is free from the isomeric meta- and para-compounds, because these salts are much more soluble in water than the ortho-salt. 20 g. of the preparation was recrystallized from 65 cc. boiling water. The product (10.5 g.) is called preparation 2.

The two preparations were analyzed by titration with sodium hydroxide and by determination of the amount of bromine which they could take up. The latter analysis was carried out in the same way as was used for aniline in an earlier paper.<sup>2</sup> One mole of *o*-chloro-anilinium chloride needs four equivalents of bromine. From the titration with sodium hydroxide the molecular weight 164.4 was found for both preparations; from the bromine titration 164.7 was found for preparation 1 and 164.1 for preparation 2. From the formula 164.0 is calculated.

The results of the electrometric measurements, which were carried out at the three temperatures 14.8°, 25.0°, and 34.9°, are given in the table. Preparation 2 was used for

<sup>1</sup> KING and ORTON, J. Chem. Soc. **99** (1911) 1381.

<sup>2</sup> PEDERSEN, J. Amer. Chem. Soc. **56** (1934) 2615.

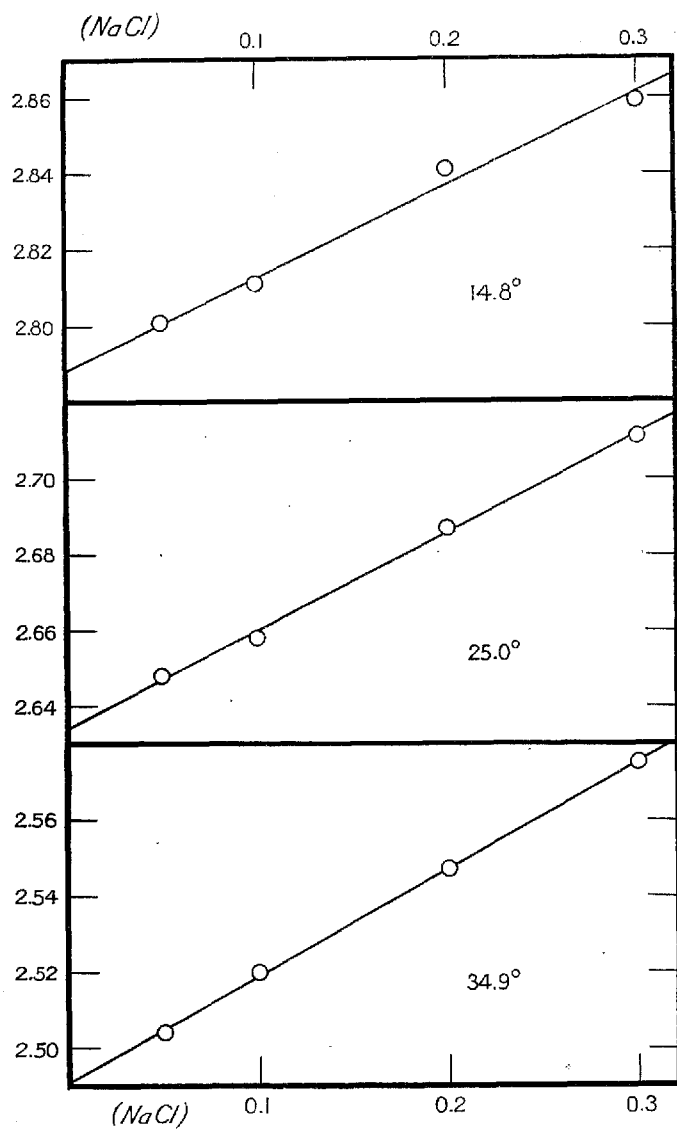


Fig. 1. The dissociation constant of the *o*-chloro-anilinium ion in sodium chloride solutions.

Table.

Electromotive force  $E$  volts of the cell
$$\text{H}_2 \left| \begin{array}{l} a \text{ molar } o\text{-Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3\text{Cl} \\ b \text{ molar } o\text{-Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 \\ (s-a) \text{ molar NaCl} \end{array} \right| \begin{array}{l} 3.5 \text{ m} \\ \text{KCl} \end{array} \left| \begin{array}{l} 0.01026 \text{ m HCl} \\ 0.0900 \text{ m NaCl} \end{array} \right| \text{H}_2$$

measured by means of the glass electrode.

	$10^3 a$	$10^3 b$	$10^3 E$	$10^3 (\text{H}^+)_1$	$-\log K - \alpha$
Temp. $14.8^\circ$ $s = 0.050$	* 25.02	24.93	47.54	1.416	2.788
	* 18.77	18.70	48.32	1.370	2.787
	* 12.51	12.46	50.35	1.290	2.796
	* 6.255	6.232	54.15	1.109	2.797
	0	0			(2.801)
Temp. $14.8^\circ$ $s = 0.100$	* 25.07	24.97	48.07	1.383	2.794
	* 18.80	18.73	49.03	1.339	2.797
	* 12.53	12.48	50.96	1.261	2.805
	* 6.267	6.242	54.58	1.087	2.804
	0	0			(2.810)
Temp. $14.8^\circ$ $s = 0.200$	25.00	25.00	49.49	1.310	2.824
	18.75	18.75	50.61	1.270	2.830
	12.50	12.50	52.13	1.200	2.832
	6.25	6.25	55.91	1.040	2.836
	0	0			(2.841)
Temp. $14.8^\circ$ $s = 0.300$	* 25.03	25.09	50.38	1.244	2.849
	* 18.77	18.82	51.28	1.208	2.852
	* 12.51	12.54	52.66	1.144	2.853
	* 6.258	6.273	56.40	0.997	2.858
	0	0			(2.859)

Table  
(continued).

	$10^3 \alpha$	$10^3 b$	$10^3 E$	$10^3 (H^+)_1$	$-\log K - \alpha$	
Temp. 25.0° $s = 0.050$	25.03	24.90	41.19	1.941	2.634	
	24.98	25.01	41.37	1.931	2.635	
	18.77	18.67	42.52	1.859	2.638	
	18.73	18.75	43.0	1.850	2.644	
	12.52	12.45	44.67	1.720	2.640	
	12.49	12.50	44.65	1.711	2.638	
	6.258	6.225	49.73	1.426	2.644	
	6.245	6.252	49.96	1.420	2.646	
	0	0			(2.648)	
	Temp. 25.0° $s = 0.100$	* 24.94	25.03	42.41	1.878	2.649
24.95		25.09	42.59	1.874	2.652	
* 18.70		18.77	43.70	1.800	2.653	
18.71		18.82	43.74	1.797	2.653	
* 12.47		12.52	45.7	1.668	2.654	
12.47		12.54	45.71	1.666	2.653	
6.238		6.272	50.64	1.387	2.657	
0		0			(2.658)	
Temp. 25.0° $s = 0.200$		25.07	25.05	43.38	1.790	2.675
		25.21	24.86	43.28	1.810	2.678
	18.80	18.78	44.56	1.719	2.677	
	18.91	18.65	44.47	1.737	2.681	
	12.53	12.52	46.62	1.598	2.681	
	12.60	12.43	46.43	1.615	2.682	
	6.268	6.263	51.29	1.338	2.682	
	6.303	6.215	51.45	1.350	2.689	
	0	0			(2.687)	
	Temp. 25.0° $s = 0.300$	26.24	25.00	43.27	1.775	2.704
19.68		18.75	44.24	1.707	2.703	
13.12		12.50	46.34	1.590	2.708	
6.56		6.25	50.89	1.337	2.710	
0		0			(2.711)	



Table  
(continued).

	$10^3 a$	$10^3 b$	$10^3 E$	$10^3(\text{H}^+)_1$	$-\log K - \alpha$
Temp. 34.9° $s = 0.050$	24.89	25.10	35.50	2.532	2.496
	18.67	18.83	37.08	2.398	2.498
	12.44	12.55	39.62	2.180	2.498
	6.222	6.275	45.8	1.746	2.503
	0	0			(2.504)
Temp. 34.9° $s = 0.100$	25.04	24.91	36.27	2.493	2.509
	18.78	18.68	37.76	2.364	2.510
	12.52	12.46	40.50	2.151	2.514
	* 6.242	6.258	46.7	1.718	2.518
	0	0			(2.520)
Temp. 34.9° $s = 0.200$	25.07	24.92	37.42	2.364	2.537
	18.80	18.69	38.82	2.246	2.538
	12.54	12.46	41.43	2.052	2.541
	6.268	6.230	47.40	1.659	2.547
	0	0			(2.547)
Temp. 34.9° $s = 0.300$	* 24.97	25.03	37.9	2.222	2.553
	24.92	24.92	38.39	2.226	2.562
	* 18.73	18.77	39.34	2.118	2.556
	18.69	18.69	39.23	2.120	2.554
	12.46	12.46	42.27	1.944	2.567
	* 6.242	6.258	48.15	1.583	2.573
	6.230	6.230	48.14	1.583	2.574
	0	0			(2.575)

most of the experiments. Only the measurements marked with an asterisk were carried out with preparation 1. The last two columns in the table contain  $(\text{H}^+)_{\text{I}}$  and  $-\log K - \alpha$ ,

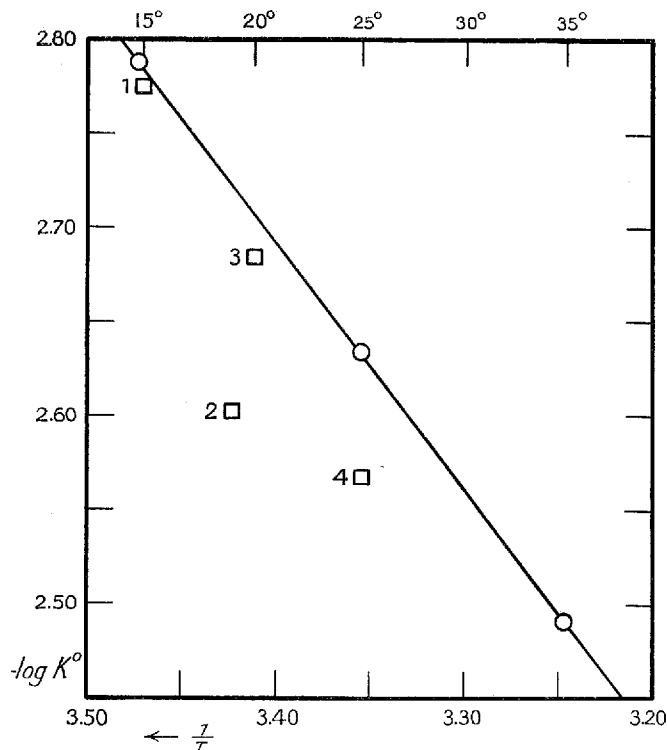


Fig. 2. The dissociation constant of the *o*-chloro-anilinium ion. Circles, this paper. Squares, other determinations.

<sup>1</sup> BRØNSTED and DUUS, catalysis. <sup>2</sup> BRØNSTED and DUUS, hydrogen electrode,

<sup>3</sup> BRØNSTED and BEHRNTS-JENSEN, hydrogen electrode. <sup>4</sup> WILLIAMS and SOPER, partition between water and benzene.

<sup>12</sup> Z. physik. Chem. **117** (1925) 299. <sup>3</sup> Private communication. <sup>4</sup> J. Chem. Soc. (1930) 2469.

computed as described above. For each series of experiments the value of  $-\log K$  for pure sodium chloride solution, found by extrapolation of  $-\log K - \alpha$  is given in parenthesis. In Fig. 1  $-\log K$  for the sodium chloride solutions is plotted against the concentration  $s$ .

The straight lines are those which are found by the method of least squares to fit closest to the points. They correspond to the following expressions for the dissociation constant  $K$  of the *o*-chloro-anilinium ion in an  $s$  molar sodium chloride solution ( $s < 0.3$ ):

$$\left. \begin{array}{l} \text{at } 14.8^\circ \quad -\log K = 2.788 + 0.243 s \\ \text{at } 25.0^\circ \quad -\log K = 2.634 + 0.260 s \\ \text{at } 34.9^\circ \quad -\log K = 2.491 + 0.281 s \end{array} \right\} \quad (5)$$

By setting  $s = 0$  we find  $K^\circ$ , the dissociation constant at infinite dilution. If we plot  $-\log K^\circ$  against  $\frac{1}{T}$ , the reciprocal of the absolute temperature, we get the points indicated by circles in Fig. 2. They fall on a straight line of equation

$$-\log K^\circ = 1.313 \frac{10^3}{T} - 1.772. \quad (6)$$

From the slope we find the heat of dissociation of the *o*-chloro-anilinium ion at infinite dilution,  $-6007$  cal./mole.

The dependence of  $K^\circ$  on the temperature may also be expressed by the following equation which is more convenient for interpolation than equation 6

$$-\log K^\circ = 2.634 - 0.0148(t - 25) + 0.00003(t - 25)^2.$$

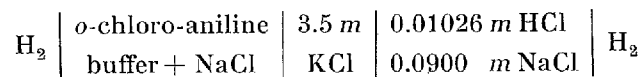
Here  $t$  is the temperature in degrees centigrade.

In Fig. 2 we have plotted both the determinations in this paper (circles) and those of other investigators (squares). The numbers refer to the list under the figure.

I wish to express my thanks to the head of the laboratory, Professor NIELS BJERRUM, for his kind interest in my work.

### Summary.

The e. m. f. of cells of the composition



were measured by means of the glass electrode at 14.8°, 25.0°, and 34.9°.

The dissociation constant of the *o*-chloro-anilinium ion at infinite dilution in 0—0.3 molar sodium chloride was calculated from the measurements (expressions 5).

From the variation with temperature the heat of dissociation of the *o*-chloro-anilinium ion at infinite dilution was calculated, and found to be —6007 cal./mole.

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